IDENTIFICATION OF INORGANICS IN THE NIST SRM1648 SAMPLE OF URBAN PARTICULATE MATTER

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ABSTRACT

X-ray diffraction, electron spin resonance (ESR) and magnetometry studies are reported on the urban particulate matter sample NIST1648. This is a time-integrated sample of urban particulate matter collected over 12 months in St. Louis. We have identified major chemical compounds present in this sample. In XRD, the sharp lines match the spectra of the following crystalline compounds: gypsum ($CaSO_4.2H_2O$), quartz (SiO_2), illite (K-Al-Si-O-OH), kaolinite (Al-Si-O-OH), zinc sulfite hydrate ($ZnSO_3.2H_2O$), zinc sulfate sulfite hydrate ($Zn_2(SO)_3(SO_4).3H_2O$), zinc arsenate hydrate ($Zn_3(AsO_4)_2.4H_2O$), and iron sulfate ($Fe_2(SO_4)_3$). Magnetometry measurements indicate the presence of Mn_3O_4, Fe_3O_4 and alpha-Fe_2O_3. In ESR spectroscopy, lines due to Fe_3O_4 and Fe^{2+} have been identified.

INTRODUCTION

Air-borne ambient particulate matter (PM) is a mixture of particles directly emitted into the air from fossil fuel combustion such as coal, oil, electrical power plants and automobile exhausts. According to the US Environmental Protection Agency (EPA), particulate matter less than 10 microns in diameter (PM_{10}) and more recently less than 2.5 microns (fine PM or $PM_{2.5}$) is of particular concern [1]. The implementation of this new rule requires the acquisition of important scientific information regarding the effects of $PM_{2.5}$ on public health and welfare. These adverse health effects include premature mortality, aggravation of respiratory and cardiovascular symptoms, change in lung structure, and altered respiratory defense mechanisms [2-4]. Two controversial studies (the Harvard University six-city study and the American Cancer Society study) have linked the presence of fine particular matter to premature mortality [5]. Generally, fine particles are considered to be more hazardous than coarse particles. Therefore, the analysis have to be done at molecular levels. In order to understand the molecular speciation and its parameters such as valency, solubility, acidity, and composition, it is essential to identify and analyze the elements and compounds present accurately by employing several analytical tools. Huggins et al., [6] have carried out x-ray absorption fine structure (XAFS) and proton induced x-ray emission (PIXE) analysis to investigate several elements in the SRM1648 urban particulate matter sample supplied by NIST (National Institute of Standards and Technology). The emphasis is placed on those elements that are either transition metals or elements defined as hazardous air pollutants in the 1990 Amendments to Clean Air Act [7].

In this paper, we present results of our investigations on the determination of the chemical compounds in the NIST standard reference material SRM1648. This sample is used as the control material in the evaluation methods used in the analysis of atmospheric particulate matter and materials with similar matrix. One of the main focus in the present work is to identify the chemical formulae of the compounds present in PM. Information on the nature of chemical compounds present in this material is essential in understanding the chemical pathways that leads to their formation. We have employed x-ray diffraction (XRD), magnetometry and electron spin resonance (ESR) spectroscopy to identify the various components present in SRM1648. Details of these results and their discussion are presented below.

EXPERIMENTAL

The sample SRM1648 of urban PM [8] was obtained from NIST. It was collected in St Louis, MO area over a 12-month period in a bag-house designed especially for the purpose. The collected particulate material was removed from the filter bags, combined into a single lot, screened through a fine-mesh sieve to remove extraneous materials and thoroughly blended in a V-blender and then packed into bottles [8].

The PIXE (proton-induced X-ray emission) spectroscopy of this sample reported by Huggins et al [6] showed the presence of Al (2.33%), Si (7.92%), S (4.55%), Ca (5.52%), Fe (3.29%) and

the elements (C,H,O,N) = 70%. Other elements present in ppm levels (shown in parenthesis) are Na (5000), Mg (5300), P (7700), Cl (4000), K (8300), Ti (3500), Zn (4130) and Pb (6720), with even smaller amounts of Cr, Mn, Ni, Cu, Br, and Sr.

The X-ray anslysis was performed using a Wide Angle X-ray Diffractometer (WAXD) from Rigaku (Model D/MAX) using Cu K ra d i ation with = 1.542 Å. The other experimental conditions include ½ degree divergence and scatter slits, 0.15mm receiving slits, step scans with 0.04 degree steps and 30sec counting time at each step, and intensity measured in counts. This relatively slow scan process enabled us to obtain the diffraction pattern with resolved sharp lines due to various compounds. The analysis of the x-ray patterns was carried out using Jade software package supplied by MDI (Materials Data Inc.) and the JCPDS data files. Magnetization measurements were done in the 5K to 350K range using a SQUID magnetometer (Quantum Design Model MPMS). ESR spectroscopy of the sample was carried out using a standard reflection type X-band spectrometer.

RESULTS AND DISCUSSION

In Figure 1 we show the x-ray diffraction pattern of the NIST SRM1648 sample. In this pattern, sharp lines due to crystalline components are superposed on a broad peak centered around 2θ = 25°. This broad peak around 25° is characteristics of amorphous carbon [10]. Using the search/match program of the Jade software together with the help of JCPDS data base, we have identified almost all the observed crystalline peaks shown in Fig. 1. They are due to gypsum ($CaSO4. 2H_2O$), quartz (SiO_2), kaolinite (Al-S-Si-O-OH), illite (K-Al-Si-O-OH), zinc arsenate hydrate ($Zn_3(AsO_4)_2. 4H_2O$), zinc sulfite hydrate ($ZnSO_3. 2H_2O$), zinc sulfate sulfite hydrate ($Zn_2(SO)_3(SO_4).3H_2O$), and iron sulfate ($Fe_2(SO_4)_3$). The major contribution of the present investigation using x-ray diffraction is that we are able to identify various compounds and their water content in this sample. In making the identifications, we compared the diffraction patterns of all apprpriate compounds available in the JCPDS files. The concentrations of the elements Al (2.33%), Si (7.92%), S (4.55%), Ca (5.52%), and Fe (3.29%) can be explained by the strong crystalline peaks in x-ray diffraction for their respective compounds mentioned above. In addition to the elemental data reported by Huggins et al. [6], x-ray diffraction analysis identifies the possible compounds present in the sample as a complimentary study. One important observation is the presence of gypsum ($CaSO_4. 2H_2O$) which is not reported in the NIST certificate of analysis. All of the compound reported here can affect human health. Quartz and the arsenic compounds may be specially hazardous [11].

Since the sensitivity of WAXD for detecting elements and compounds in a mixture is at best limited to individual concentrations of 1% or more, we have employed magnetometry and ESR spectroscopy for possible detection of other materials. In Fig. 2, temperature variation of the magnetization of the sample SRM 1648 is shown. The arrows indicate the positions where magnetic transitions due to Mn_3O_4 (T_c= 43 K[12]), Fe_3O_4 (T_c = 120 K) and alpha-Fe_2O_3 (T_c =260 K) are known [13]. In order to confirm these assignments, a laboratory prepared mixture of Fe_3O_4, Mn_3O_4 and alpha-Fe_2O_3 in 1:1:1 ratio by weight was investigated (Fig. 2) by magnetometry. The transition temperatures observed in SRM1648 match with the three oxides, confirming our identifications. The concentration of Mn_3O_4 is relatively small in SRM1648 as indicated by the weakness of the peak near 43K. The results obtained by magnetometry provide evidence for the usefulness of this technique for detecting ferrimagnetic and ferromagnetic materials in quantities too small to be detected by x-ray diffraction.

The ESR spectroscopy of SRM1648 carried out room temperature and at 9.2GHz shows several lines (Fig.3). The main line with g = 2.2 and linewidth ΔH = 688 G is probably due to Fe_3O_4. The line at g = 3.57 (Fig.4) matches the location expected for Fe^{2+} species in octahedral symmetry [14]. The remaining lines are clearly a part of the hyperfine structure. However because of lack of resolution, we are not able to identify all the lines and hence their origin at this time remains unresolved. Perhaps, with variable temperature ESR spectroscopy, we might be able to resolve this issue in the near future.

In summary, with the combined use of WAXD, magetometry and ESR spectroscopy, we have been able to identify a significant number of chemical compounds present in the NIST SRM1648 sample of urban particulate matter. This information combined with the data available from PIXE and XAFS on the elemental concentrations [6] provides a nearly complete analysis of the major constituents of this sample.

REFERENCES

1. Federal Register, 62 FR 38652, July 18, 1997.
2. D. W. Dockery, C. A. Pope, X. Xu, J. D. Spengler, J. H Ware, M. E. Fay, B. G. Ferris, and F. E. Speizer, New England J. Med., 329 (1993) 1753.
3. R. T. Burnet, R. Dales, D. Krewski, R. Vincent, T. Dann, and J. R. Brook, Am. J. Epidemiology, 142 (1995) 15.
4. J. Schwartz, and R. Morris, Am. J. Epidemiology, 142 (1995) 23.
5. Chemical Engineering News, Particulate Matter Health Studies to be Reanalyzed August 18, (1997) 33.
6. F. E. Huggins, G. P. Huffman, and J. D. Robertson, J. Haz. Mat. (in press)
7. Amendments to Clean Air Act, U.S. Public Law 101-549, U.S. Gov. Printing Office, 1990, 314 pp.
8. National Institute of Standards & Technology, Certificate of Analysis, Standard Reference Material 1648, Urban Prticulate Matter, August 30,1991, 5 pp.
9. V. S. Babu, L. Farinash and M. S. Seehra, J. Mater. Res., 10, 1075 (1995).
10. A. Manivannan, M. Chirila, N. C. Giles and M. S. Seehra, Carbon 37 (1999) 1741.
11. R.S. Pandurangi, M. S. Seehra, B. L. Razzaboni and P. Bolsaitis: Environ. Health Perspectives, 86 (1990) 327.
12. G. S. Chaddha, and M. S. Seehra, J. Phys D: Appl. Phys. 16 (1983) 1767.
13. G. Srinivasan and M. S. Seehra, Phys. Rev. B (1983) 1.
14. Paramagnetic Resonance in Solids by W. Low (Academic Press, NY 1960) p. 87.
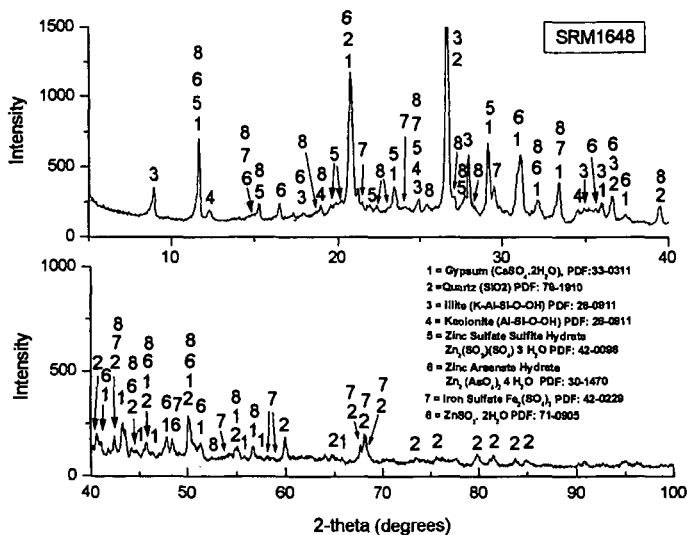
Figure 1. Room temperature x-ray diffractogram of the NIST SRM1648 sample. Lines due to various crystalline components are identified. The broad background near $2\theta \sim 25°$ is due to amorphous carbon.
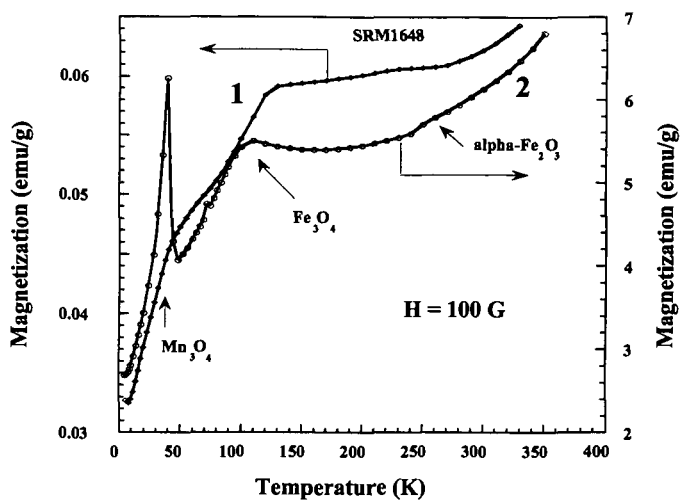
Figure 2. Temperature variation of the magnetization for SRM1648 (data 1) and for a laboratory prepared mixture of Fe_3O_4, Mn_3O_4 and alpha-Fe_2O_3 (1:1:1) (data 2). The transition temperatures indicated by arrows observed for the mixture are also observed in SRM1648.
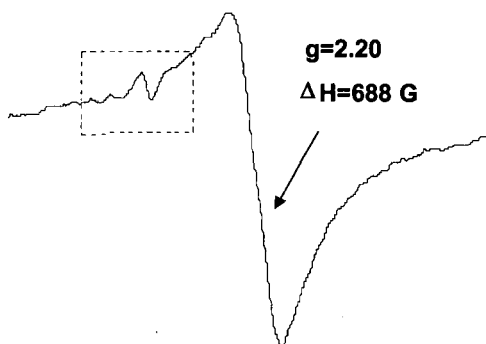

Figure 3. Room temperature ESR spectrum of SRM1648. The line shown by arrow at $g = 2.2$ is probably due to ferrimagnetic Fe_3O_4.
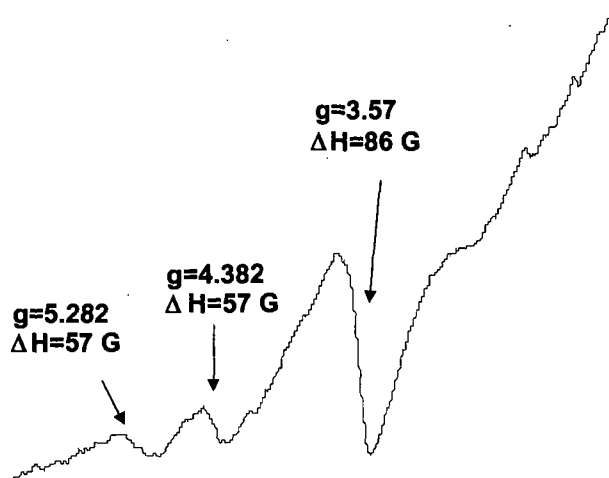
Figure 4. Expanded ESR spectrum of the box area shown in Figure 3. For some of the lines g and ΔH values are indicated. See text for details.